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Moyer

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[54] **METHODS AND COMPOSITIONS FOR REFINING BITUMINOUS FROTH RECOVERED FROM TAR SANDS**

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[51] **Int. Cl.** **B01d 17/04**

[58] **Field of Search** 252/331, 349, 358, 364; 208/11, 45; 106/278

[56] **References Cited**

UNITED STATES PATENTS

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FOREIGN PATENTS OR APPLICATIONS

596,561	4/1960	Canada	208/11

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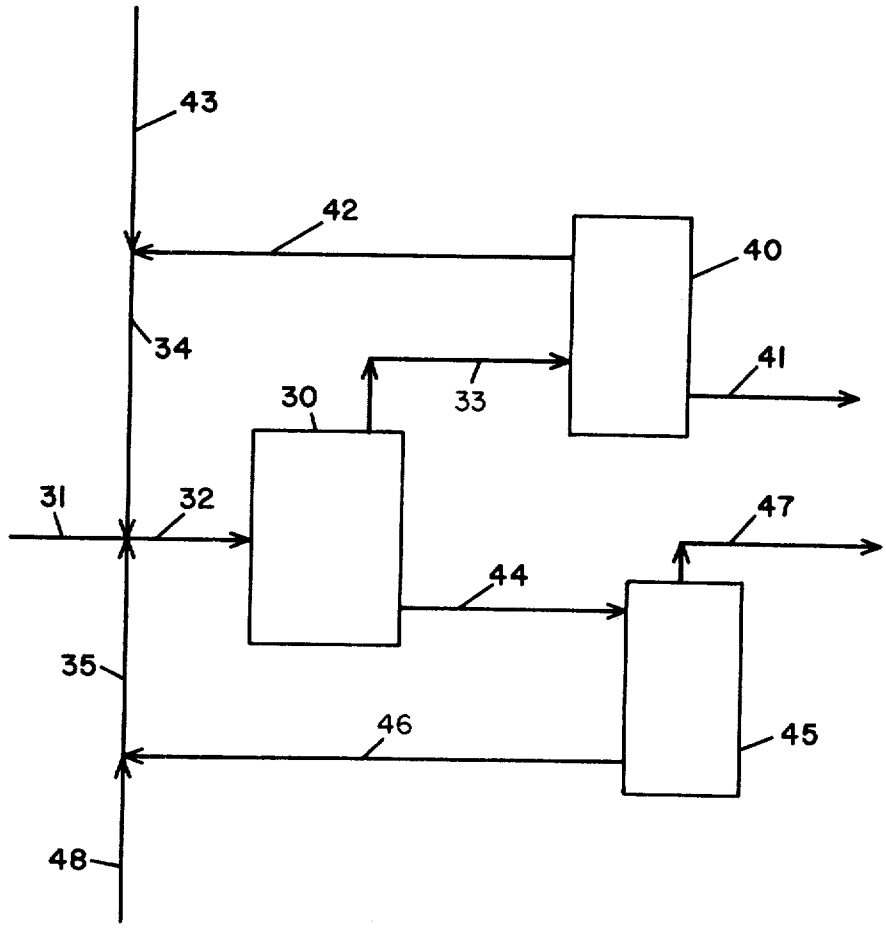
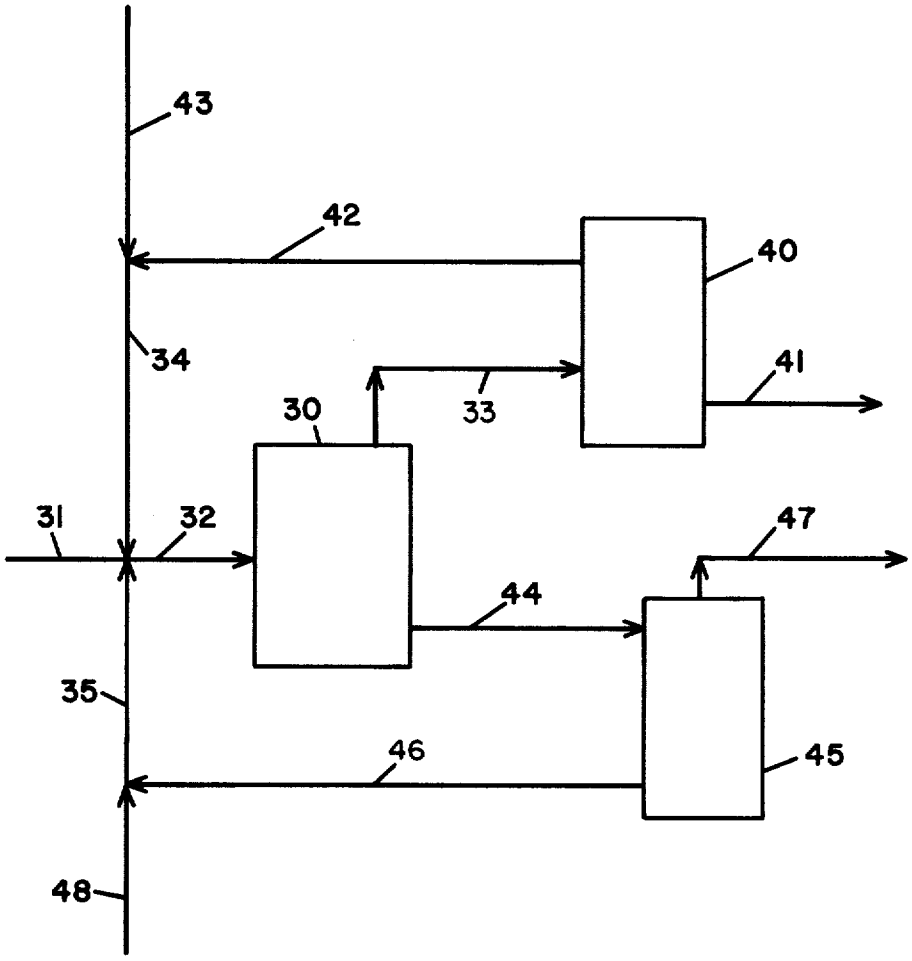
[57] **ABSTRACT**

A method for refining emulsion-containing bituminous froth having water and mineral matter impurities recovered from tar sands via hot water extraction comprising adding a deemulsifying quantity of a C_3 to C_7 ketone to the froth and thereafter centrifuging the froth-ketone mixture to provide a froth product substantially reduced in water, mineral matter and emulsions.

10 Claims, 1 Drawing Figure

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METHODS AND COMPOSITIONS FOR REFINING BITUMINOUS FROTH RECOVERED FROM TAR SANDS

BACKGROUND OF THE INVENTION

The present invention relates to the hot water extraction process for recovering bitumen from tar sands. More particularly, the present invention relates to an improvement in the diluent composition added to bituminous froth recovered from tar sands via hot water methods of extraction. Specifically, the present invention provides methods and compositions which improve the process of separating from bituminous froth impurities such as water and mineral matter normally associated with bituminous froth recovered from tar sands by the hot water extraction technique.

The tar sands are primarily silica, having closely associated therewith an oil film which varies from about 5 percent to 21 percent by weight, with a typical content of 13 weight percent of the sand. The oil is quite viscous—6° to 8° API gravity—and contains typically 4.5 percent sulfur and 38 percent aromatics.

The sands contain, in addition to the oil and sand components, clay and silt in quantities of from 1 to 50 weight percent, more usually 10 to 30 percent. The sands also contain a small amount of water, in quantities of 1 to 10 percent by weight, in the form of a film around the sand grains.

Several basic extraction methods have been known for many years for the separation of oil from the sands. In the so called "cold water" method, the separation is accomplished by mixing the sands with a solvent capable of dissolving the bitumen constituent. The mixture is then introduced into a large volume of water, water with a surface agent added, or a solution of a neutral salt in water, which salt is capable of acting as an electrolyte. The combined mass is then subjected to a pressure or gravity separation.

In the hot water method, as disclosed in Canadian Pat. No. 841,581 issued May 12, 1970, the bituminous sands are jetted with steam and mulled with a minor amount of hot water at temperatures of 170° to 190° F., and the resulting pulp is then dropped into a turbulent stream of circulating hot water and carried to a separation cell maintained at a temperature of about 185° F. In the separation cell, sand settles to the bottom as tailings and oil rises to the top in the form of a froth. An aqueous middlings layer comprising clay and silt and some oil is found between these layers. This basic process may be combined with a scavenger step for further treatment of the middlings layer obtained from the primary separation step to recover additional amount of oil therefrom.

The scavenger step may be conducted on the middlings layer from the primary separation step to recover additional amounts of bitumen therefrom. This step usually comprises aerating the middlings as taught by K. A. Clark. "The Hot Water Washing Method," Canadian Oil and Gas Industries 3, 46 (1950). These froths are then combined, diluted with naphtha and centrifuged to remove more water and residual mineral. The naphtha is then distilled off and the bitumen is coked to a high quality crude suitable for further processing.

The butumen product from this hot water process is in the form of an aerated froth of a very specific composition. The product contains 35 to 45 volume percent water and 5 to 10 volume percent mineral before

dilution. A substantial quantity of the bitumen and water is found to be in the form of tight emulsions when the froth is recovered. The water content of this froth product must be reduced to 4 to 6 volume percent and the mineral to 1 to 2 weight percent before the product can be further processed. This reduction can be accomplished by plural stage centrifuging as described in Hall et al., Canadian Pat. No. 910,271 issued Sept. 19, 1972, or as in Canadian Pat. No. 596,561 issued Apr. 19, 1960 to Coulson.

Each stage of the centrifuging operation can consist of a single machine or each stage can comprise a battery of units connected in parallel. In these operations the first stages are conducted by the application of relatively low forces to remove larger mineral while relatively higher forces are applied in the later stages to remove the smaller mineral and most of the water. The mineral and water discharged from the centrifuges are normally removed from the centrifuging zone for disposal.

DESCRIPTION OF THE INVENTION

It has now been discovered that the method of purifying bitumen froth by centrifuging the froth to remove water and mineral matter can be substantially enhanced by the addition of a C_3 to C_7 ketone to the froth prior to the centrifuging procedure. Specifically, it has been discovered that by the addition of a C_3 to C_7 ketone to a petroleum naphtha diluent which is thereafter added to the bitumen froth, the efficiency of the centrifuging step is substantially improved to provide a bitumen product having a substantial quantity of the water and mineral impurities removed. Thus an improved bitumen product suitable for further refining into a synthetic crude oil product is provided.

As disclosed above, the bituminous froth suitable for use in the method of the present invention is the froth product recovered by way of the hot water extraction process for the recovery of bitumen from tar sands. As hereinafter disclosed all percentages are by volume unless otherwise provided. The froth product can contain 20 to 60 percent water and normally contains 35 to 45 percent water before dilution. The froth also can contain 1 to 10 percent mineral matter which can vary in size from coarse sand particles which will not pass through a 325 mesh screen to fine clay particles smaller than 2 microns. Normally the froth contains 1 to 5 percent mineral matter.

A liquid hydrocarbon which is generally used to dilute bitumen froth prior to the centrifuging step can be a coker distillate naphtha boiling in the range of 150° to 500° F. with 50 percent of the naphtha boiling below 300° F. The naphtha can be a hydrogenated naphtha distillate product. Generally, the naphtha can be characterized as containing 5 to 50 volume percent aromatic hydrocarbons, 0 to 50 volume percent olefins and 50 to 95 volume percent saturated hydrocarbons. Naphtha is added to the bitumen froth in the range of 0.25 to 4.0 volumes of diluent per volume of bitumen froth. The preferred ratio of diluent to froth is one to one. The quantity of ketone added to the froth is normally in the range of 5 to 25 volume percent.

The ketone additives of the methods and compositions of the present invention are the C_3 to C_7 ketones including acetone, 2-butanone, 2-pentanone, 3-pentanone, 2-hexanone, 3-hexanone, 2-heptanone and 3-heptanone. The ketone used should be at least

slightly soluble in water. The preferred ketones usable in the present invention are acetone and 2-butanone. As a practical matter, the ketone additive should have a boiling point lower than 500° F. The C_3 to C_5 ketones including acetone, 2-butanone, 2-pentanone and 3-pentanone are the preferred ketone additives in the method and compositions of this invention.

To more clearly define the method of the present invention, the drawing is provided. Referring to the drawing, a bituminous froth feed material recovered from tar sands via hot water extraction and containing water and mineral impurities is provided via line **31** and transferred into line **32** where it is mixed with naphtha diluent from line **34** and a C_3 to C_7 ketone from line **35.** The diluted froth is transferred into centrifuge zone **30.** By the centrifuging procedure the froth feed is divided into a bitumen froth product stream and a water mineral matter stream. The water and mineral stream is withdrawn via line **44** and transferred into stripping zone **45.** In stripping zone **45** naphtha diluent containing the ketone deemulsifying agent is stripped from the water and mineral matter fractions via distillation and the distillate is transferred via line **46** to feed line **35** where the recovered diluent is added to make up ketone provided by line **48.** Water and mineral matter are recovered from stripper zone **45** via line **47** and can be discarded.

Diluted bituminous froth substantially free of water and mineral matter is transferred from centrifuging zone **30** to diluent recovery unit (DRU) **40** via line **33.** Diluent is recovered from the DRU via line **42** and transferred to line **34** where it can be combined with make up diluent from line **43** prior to addition to the froth feed in line **32.** The bitumen froth product substantially reduced in water and mineral matter is recovered from DRU **40** via line **41** and further processed to a synthetic crude oil product by means not shown but disclosed in the art.

One of the major difficulties in purifying the bitumen froth recovered from tar sands via the hot water extraction process is the removal of water from the bitumen-water emulsions of the froth. The efficiency of the centrifuge is greatly reduced when the froth is substantially in the emulsified form as is common with some froth product recovered from the hot water process as hereinabove disclosed. One approach to this problem has been the addition of inorganic deemulsifying compounds. This approach has proven to be technically successful but very expensive in a large scale commercial plant. The inorganic additive is normally lost in the process and cannot be recycled. In some instances, and in particular with the use of inorganic deemulsifying agents, the additive remains in the bitumen product to in effect provide another impurity in the froth product. An added advantage of the present invention is that ketone additives used herein are recoverable and recyclable. Also the ketones are compatible with both the bitumen froth and the naphtha diluent.

Thus by the method of the present invention as is illustrated in the drawing the ketone deemulsifying agents of the present invention can be recovered with naphtha diluent and recycled within the bituminous froth purifying process thereby providing substantial economic advantages over other methods practiced in the art.

In addition the present invention provides an improved process for removing water and mineral matter impurities and deemulsifying bitumen froth recovered via hot water extraction of bitumen from tar sands which froth is partially emulsified and contains water and mineral matter which comprises adding a deemulsifying quantity of a C_3 to C_7 ketone to the froth.

In essence the present invention also provides novel liquid diluent compositions suitable for addition to bitumen froth to lower the specific gravity and improve the flow characteristics of the froth to make it suitable for upgrading by centrifuging. A new petroleum naphtha diluent characterized as containing 20 to 80 volume percent of naphtha comprised of 5 to 50 percent aromatic hydrocarbons, 0 to 50 percent olefins, 50 to 95 percent saturated hydrocarbons and 20 to 80 percent C_3 to C_7 ketone has been discovered as being particularly effective to dilute bituminous froth containing water and mineral matter impurities. It has been discovered that the above novel froth diluent is particularly useful in improving the processability of the froth. Specifically, water and mineral matter are more easily and efficiently removed from the bituminous froth when it is diluted with this novel diluent and thereafter subject to a centrifuging process.

Also, the present invention provides a bituminous froth composition suitable for refining to a synthetic crude oil comprising:

a. 20 to 80 percent by volume of a froth containing
   i. 35 to 45 percent water,
   ii. 1 to 10 percent mineral matter and
   iii. 45 to 60 percent bitumen and
b. 20 to 80 weight percent liquid diluent containing
   i. 20 to 80 percent C_3 to C_7 ketone and
   ii. 20 to 80 percent of a petroleum naphtha characterized as boiling in the range of 150° to 500° F. and comprising 5 to 50 volume percent aromatic hydrocarbons, 0 to 50 volume percent olefins and 5 to 95 volume percent saturated hydrocarbons.

EXAMPLE I

A liter of bituminous froth containing 38 volume percent water and 4 volume percent mineral matter is diluted with 500 milliliters of petroleum naphtha having a boiling range of 150° to 480° F. The mixture is agitated until substantially homogeneous and subsequently a 100 milliliter aliquot is withdrawn and subject to centrifugal forces for 20 minutes in a centrifuge rotating at 1,700 RPM. The aliquot is observed to separate into three separate phases which are 1 milliliter of solids, 15 milliliters of water and 84 milliliters of froth.

EXAMPLE II

A bituminous froth identical to the froth of Example I is prepared in the same manner with the exception that the naphtha diluent contains 50 volume percent acetone. The froth is thereafter centrifugal as in Example I. The product after centrifuging comprises three phases which are 3.5 volume percent mineral matter, 34 volume percent water with some acetone dissolved therein and the remainder froth.

By this example the improvements achieved by the methods and compositions of the present invention are clearly demonstrated. Any of the herein disclosed C_3 to C_7 ketones can be substituted for the acetone in the example with substantially equivalent results being obtained.

In one aspect, the present invention comprises a method for upgrading bituminous froth containing water and mineral impurities which comprises diluting the froth with petroleum naphtha containing 10–50 percent by volume of a C_3–C_7 ketone and thereafter centrifuging the diluted froth and recovering a froth product substantially free of emulsions and substantially reduced in water and mineral matter.

The invention claimed is:

1. An improved diluent suitable for improving the processability of bituminous froth consisting of:

a. 20 to 80 percent petroleum naphtha characterized as boiling in the range of 150° to 500° F. and containing 5 to 50 percent aromatic hydrocarbons, 0 to 50 percent olefins, 50 to 95 percent saturated hydrocarbons and

b. 20 to 80 percent of a C_3 to C_7 ketone and mixtures thereof.

2. A composition according to claim **1** wherein said ketone is selected from the group consisting of acetone, 2-butanone, 2-pentanone and 3-pentanone.

3. A method for upgrading emulsion containing bituminous froth containing water and mineral impurities which comprises diluting the froth with petroleum naphtha containing 10 to 50 percent by volume of a C_3 and C_7 ketone and thereafter centrifuging the diluted froth and recovering a froth product free of emulsions and substantially reduced in water and mineral matter.

4. A method for upgrading a bitumen froth recovered from tar sands via hot water extraction process which comprises:

a. mixing said bituminous froth containing 35 to 45 percent water and 1 to 5 percent mineral matter with a petroleum naphtha boiling in the range of 150° to 500° F. and containing 10 to 50 percent C_3 to C_7 ketones,

b. centrifuging the froth-diluent mixture and

c. recovering a diluted bitumen froth substantially free of emulsions and substantially reduced in water and mineral matter.

5. A method according to claim **3** wherein the ketone is selected from the group consisting of acetone, 2-butanone, 2-pentanone and 3-pentanone.

6. A method according to claim **4** wherein the ketone is selected from the group consisting of acetone, 2-butanone, 2-pentanone and 3-pentanone.

7. A method for upgrading emulsion containing bituminous froth containing water and mineral impurities comprising:

a. adding to the froth a liquid diluent characterized as containing

i. 20 to 80 volume percent of a C_3 to C_7 ketone and mixtures thereof and

ii. 20 to 80 volume percent of petroleum naphtha characterized as boiling in the range of 150° to 500° F. and containing 5 to 50 percent aromatic hydrocarbons, 0 to 50 percent olefins and 50 to 95 percent saturated hydrocarbons;

b. centrifuging said froth and

c. recovering a froth product substantially free of emulsions and substantially reduced in water and mineral matter.

8. A method according to claim **7** wherein said emulsion containing bituminous froth is recovered via hot water extraction from tar sands and contains 35 to 45 percent water and 1 to 5 percent mineral matter.

9. A method according to claim **7** wherein the ketone is selected from the group consisting of acetone, 2-butanone, 2-pentanone, and 3-pentanone.

10. A method according to claim **8** wherein the ketone is selected from the group consisting of acetone, 2-butanone, 2-pentanone, and 3-pentanone.

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